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Ordered Semiconducting Self-Assembled Monolayers on Polymeric Surfaces Utilized in Organic Integrated Circuits

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ABSTRACT We report on a two-dimensional highly ordered self-assembled monolayer (SAM) directly grown on a bare polymer surface. Semiconducting SAMs are utilized in field-effect transistors and combined into integrated circuits as 4-bit code generators. The driving force to form highly ordered SAMs is packing of the liquid crystalline molecules caused by the interactions between the linear alkane moieties and the $\pi-\pi$ stacking of the conjugated thiophene units. The fully functional circuits demonstrate long-range order over large areas, which can be regarded as the start of flexible monolayer electronics.

KEYWORDS Self-assembled monolayer field-effect transistors, self-assembly, organic integrated circuits, liquid crystal, organic dielectric

The realization of the first chemisorbed self-assembled monolayers (SAMs) in the 1980s inspired many to study its formation and characterize its properties.[1,2] Since then, SAMs are applied to, e.g., change the wetting properties of materials,[3] adapt the work function of metals,[4,5] build large-area molecular junctions,[6] or fabricate ultrathin dielectrics.[7,8] Self-assembly is advantageous from a technological point of view because it is one of the few practical strategies for making ensembles of nanostructures.[9] In self-assembled monolayer electronics, the basic building block is the self-assembled monolayer field-effect transistor (SAMFET), in which the semiconductor is a single molecular layer spontaneously formed on the gate dielectric. Recently the first SAMFETs were reported and combined into integrated circuits. The demonstration of real logic functionality makes self-assembly the ultimate technology for bottom-up mass production of organic electronics. However, up to now SAMFETs were made using thermally grown SiO_2 as the gate dielectric.[10] The high processing temperature prevents a direct transfer of the existing technology to the application in flexible electronics. Processing on foil has a limited temperature budget of about 200 °C. Therefore a prerequisite to incorporate SAMs as active layers in flexible electronics is to grow ordered monolayers on organic dielectrics processed at low temperatures.

SAM formation on metals and oxides has been studied extensively.[3] Monolayers of thiols on gold grow dynamically, while silane SAMs on SiO_2 grow through the development of islands.[11] In general, SAMs cannot be directly formed on a blank, i.e., unmodified, polymer surface.[12] A buffer layer is necessary to act as a bridge between the polymer surface and the SAM. For instance polyethylene and poly(dimethylsiloxane) have first been functionalized with a thin silicate layer onto which the actual SAM has been formed.[13] Additionally (aminopropyl)triethoxysilane was grafted as a buffer layer on poly(ethylene terephthalate).[12] Little is known about the growth mechanism.[13] Only recently it was shown that silane molecules can stick to a blank rubrene surface.[14] However highly ordered densely packed SAMs on polymers have not yet been reported.

To create *semiconducting* SAMs on an organic dielectric, the formation of a monolayer itself is not sufficient. In a monolayer transistor the layer thickness is comparable to that of the accumulation layer. In that case, structural imperfections, as voids or grain boundaries, lead to a deteriorated charge carrier mobility. Hence, efficient charge transport can only occur when the SAM is highly ordered. Here, we show that semiconducting SAMs not only are able to grow on organic dielectrics but also exhibit long-range order and allow for charge transport over micrometer distances. Our SAMFETs comprising an organic dielectric

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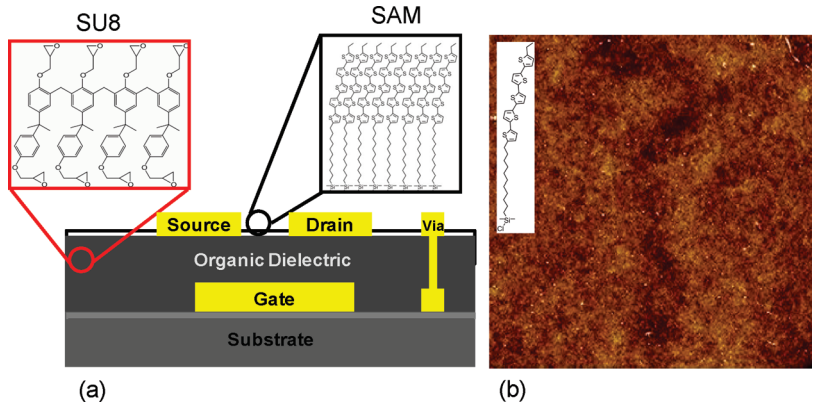

FIGURE 1. Schematic cross section of a SAMFET with an organic dielectric. (a) From bottom to top: a rigid monitor wafer, gold gate line, organic dielectric, gold source−drain electrodes, and SAM. (b) AFM topography of the monolayer grown on the organic dielectric ($9 \times 9\ \mu m^2$), the z axis is 25 nm. The inset shows the chemical structure of the molecule.

exhibit the same performance as their hybrid, SiO_2 based, counterpart. Subsequently over a hundred SAMFETs were integrated into self-assembled monolayer circuits. The functional circuit, processed at low temperature, paves the way for flexible self-assembled monolayer electronics. We speculate that the origin for the formation of the highly ordered SAM on the blank polymer substrate is the liquid crystalline nature of the molecules employed.

Self-assembled monolayer field-effect transistors are fabricated in a bottom-gate, bottom-contact architecture, as illustrated in Figure 1a. First, a 50 nm Au layer is deposited onto the substrate and patterned using standard photolithographic and wet etching techniques to build the transistor gate and a first interconnect layer. An epoxy-based negative photoresist, SU8, is then spin-coated onto the wafer acting as the gate dielectric. Instabilities in the surface of the dielectric may occur because the molecules are mobile and the surface can resemble a viscous fluid.[15] To prevent instabilities such as swelling, we cross-linked the photoresist. The generic chemical structure is shown in the inset of Figure 1a. SU8 was chosen because it is a well-studied compound used in electronics[16,17] and, most importantly, because it contains epoxy groups, which are easily converted to −OH groups upon exposure to an oxygen plasma. Subsequently to the deposition of the gate dielectric, holes are photochemically defined to form the vertical interconnects (vias). A second Au layer is deposited on the stack and patterned to define the source and drain contacts together with a second interconnect layer.[18]

As semiconducting molecules we use chloro[11-(5‴″-ethyl-2,2′:5′,2″:5″,2‴:5‴, 2‴″-quinquethien-5-yl)undecyl]-dimethylsilane as described previously.[10] The chemical structure of the self-assembled molecules is shown as inset in Figure 1b. However, the molecules do not have a chemical interaction with the cross-linked polymeric gate dielectric. To impose a driving force toward self-assembly, the gate dielectric was activated using an oxygen plasma. The activated surface was hydrolyzed by submerging the substrate in water. The functional groups formed by the plasma

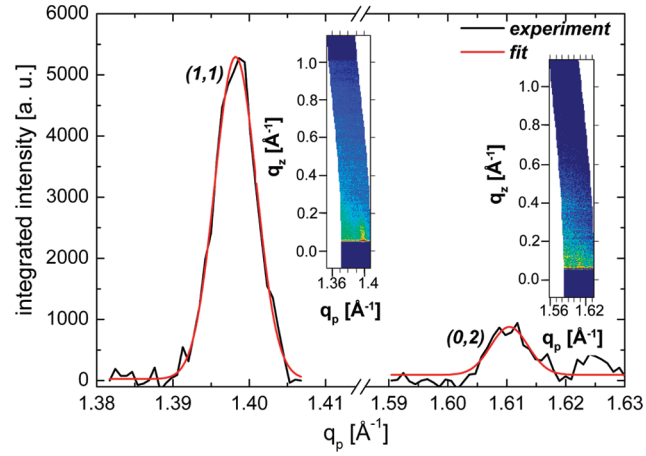

FIGURE 2. Grazing-incidence diffraction measurements. The diffracted intensity integrated over the q_z direction, corrected for background as a function of in-plane scattering vector q_p. The black line represents the actual measurement whereas the red line shows a fit to the experimental data to determine the exact peak position. The insets show the diffraction intensity from the Bragg rods in their reciprocal space maps. The (1,1) and (0,2) reflection are indicated.

treatment are undoubtedly heterogeneous in both type and distribution.[19] We did not optimize the processing conditions to obtain the highest number of silanol groups as reported to be crucial for SAM formation on SiO_2. After the water treatment, the substrate was blow dried and put in a dry toluene solution containing the active molecules for 2 days. The devices were finished upon annealing in vacuum (10^{-5} mbar) at 130 °C to remove traces of solvent.

The microstructure of the SAM was investigated by grazing incidence X-ray diffraction. Figure 2 shows the diffracted intensity integrated over the q_z direction, corrected for the background intensity from the polymer substrate underneath. The black line shows the integrated values whereas the red line shows a fit to the experimental data to determine the exact peak position. The diffracted intensity is presented as a color map in the inset of Figure 2 as a function of perpendicular and in-plane scattering vectors, q_z and q_p. The

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horizontal line at $q_z = 0.06$ Å^{-1} is due to diffuse scattering from the sample surface at the critical angle as described by Yoneda.[20] Most important are the vertical lines, the so-called Bragg rods.[21] They demonstrate in-plane order arising from the thiophene units; the rod shape arrives from the absence of periodicity perpendicular to the SAM.

The Bragg rods of the monolayer are well-defined, but they show low scattering intensity because of the remaining strong background intensity from the polymer substrate underneath. Due to the very low electron density contrast between the polymer substrate and the monolayer itself, a very poor peak to background ratio is found. The small in-plane width of the rods is a clear evidence of high order and large crystalline 2D domains within the monolayer. From the peak positions a rectangular unit cell can be determined which contains two molecules in a herringbone packing that is comparable to reported crystal structures of oligothiophenes.[22] The Bragg rods can be indexed as the (1,1) and (0,2) reflections of a rectangular unit cell with lattice constants $a = 5.49$ Å and $b = 7.81$ Å, identical to the values previously obtained for SAM formation on SiO_2.[23] The shape of the Bragg rods in reciprocal space (decay of the intensity along q_z at constant q_p) shows upright standing molecules because the maximum intensity occurs at the Yoneda reflection.[20]

The chemical composition was studied by X-ray photoelectron spectroscopy (XPS) as described in the Supporting Information. The quantitative analysis of the XPS showed that the layer thickness of the SAM is 2.9 nm assuming a densely packed monolayer and is in agreement with the calculated length of the molecule. The morphology was investigated by atomic force microscopy (AFM) measurements on different spots on the sample. A typical spatial map of the topography is presented in Figure 1b showing a fully covered smooth monolayer. If present, bilayers or voids could easily have been resolved.[23] We note that a smooth surface alone could be due to the absence of molecules. To explicitly establish the presence of the semiconducting molecules, the electrical transport was characterized. A typical transfer characteristic of a transistor with concentric source and drain contacts, a channel length of 20 μm, and a channel width of 1000 μm is shown in Figure 3a. The extracted device mobility for linear and saturation regime is about 0.02 cm^2 V^{-1} s^{-1}, identical to the mobility obtained in SAMFETs comprising SiO_2 as gate dielectric.[10] The observed gate-controlled modulation of the source-drain current, in combination with the AFM measurements taken in the transistor channel is a direct evidence for the presence of the formation of a semiconducting self-assembled monolayer on the organic gate dielectric.

The SAMFETs exhibit a positive threshold voltage. Any integrated circuits comprising these transistors should therefore be based on "$V_{gs} = 0$" logic,[18,25] using inverters with the gate of the load shorted with the source. The basic operation of the inverter can be interpreted as a voltage

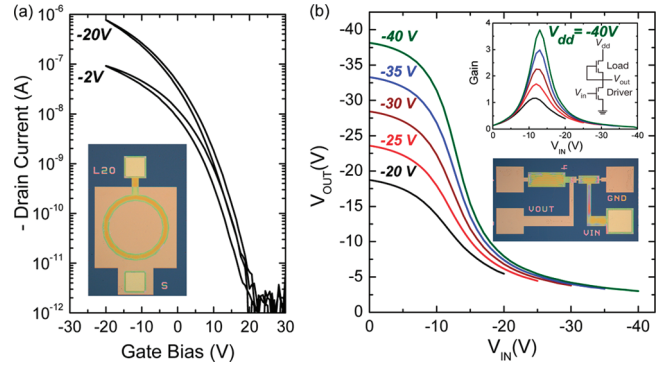

FIGURE 3. (a) Transfer characteristic of a SAMFET with concentric source and drain employing a organic dielectric. The inset shows a photomicrograph of the transistor. (b) Input−output characteristic of an inverter for different supply voltages. The inset shows the signal gain as a function of V_{in} measured at different supply voltages V_{dd}, color coded as the main panel and a photomicrograph of the voltage inverter.

divider controlled by the input voltage. When the input voltage is low ($V_{in} = V_{dd}$), the driver transistor is turned on and the output voltage is pulled up from logic 1 to logic 0.[24,25] When the input voltage is high ($V_{in} = 0$), the output voltage is pulled down to V_{dd} because the load transistor is chosen much wider than the driver. Figure 3b shows the output signal of the inverter as a function of the input voltage (V_{in}). Voltage inversion is observed. The inset of Figure 3b illustrates the output gain as a function of V_{in}, measured at different supply voltages. The observed gain is similar to the one obtained in conventional thin film organic inverters[25] and inverters based on SAMFETs with a SiO_2 gate dielectric.[10]

Inverters were combined into seven-stage ring oscillators. A buffer stage was added to determine the switching frequency. The ring oscillators were measured at a supply voltage of −32 V over a resistor with an oscilloscope. An oscillation frequency, f, of about 2 kHz was obtained as shown in Figure 4a. Realization of real logic functionality requires a small parameter spread in mobility and threshold voltage. We combined over a hundred SAMFETs using polymeric dielectric in 4-bit code generators in which the ring oscillators act as the clock generator. The code generator also contains hard-wired memory, a four-bit counter, decoder logic, and a load modulator. The output of the code generator is presented in Figure 4b. The bit rate is around 0.5 kbit/s at a supply voltage of −42 V. The circuit performance is similar to that of state-of-the-art organic integrated circuits developed for organic radio frequency identification transponders.[26]

By now it is well established that at room temperature alkanesilane SAMs on SiO_2 grow in islands.[11] The silane molecules are first physisorbed at the hydrated silicondioxide surface, where hydrolysis of the SAM molecules takes place. Via a condensation reaction the SAM covalently binds to the interface. The self-assembly can be driven by the lipophilic interactions between the linear alkane moieties

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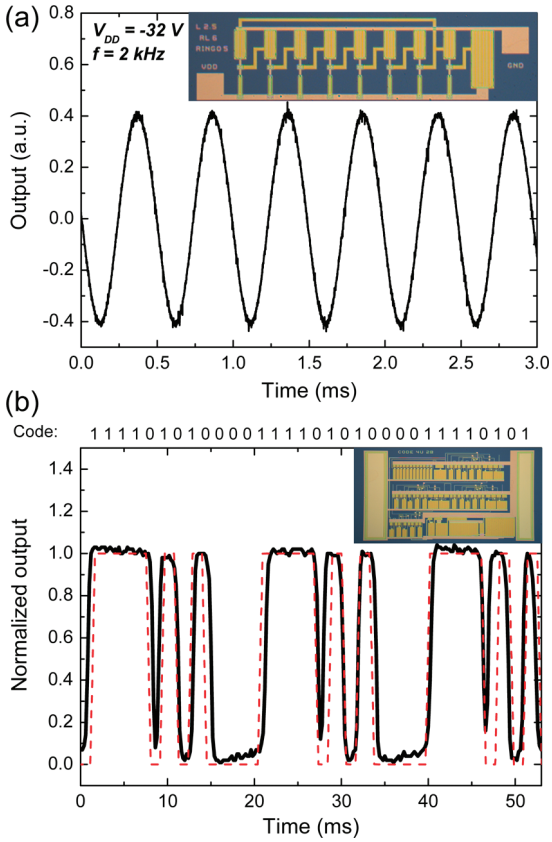

FIGURE 4. (a) Output signal of a seven-stage ring oscillator measured at a supply voltage of −32 V. The inset shows an optical micrograph. (b) Output of a 4-bit code generator. The preprogrammed code is indicated above the diagram and by the red dotted line. The inset shows again an optical photomicrograph.

and by the enthalphic van der Waals forces. In the initial period the monolayer grows in a disordered liquid-like state and, with time, islands grow laterally and their size is limited by diffusion. The surface coverage increases until a densely packed fully ordered SAM is obtained. In our case, the self-assembling molecule consists of an aliphatic chain and a thiophene core each having the possibility to drive the self-assembly. On SiO_2, the growth mechanism has been studied by AFM and SKPM measurements on partially and fully formed monolayers. Incomplete monolayers grow in islands comparable to alkanesilanes on SiO_2. The electrical connection in between grains, with possibly different crystallographic orientations, was shown not to hamper the electrical transport.[23] On SU8, in complete monolayers imperfections as voids could not be identified. The electrical transport measurements discussed above show a comparable performance to SAMFETs optimized with SiO_2 as gate dielectric.

We tentatively explain the occurrence of highly ordered densely packed SAMs directly on a polymeric surface as follows: first a few anchoring points are made by plasma oxidation. The monodentate molecules physisorb on the hydrated surface where they can covalently bind and subsequently grow into a compact SAM. The driving force is packing of the liquid crystalline molecules caused by the interaction between the linear alkane moieties and the $\pi-\pi$ stacking of the conjugated thiophene units. Defects due to uncontrolled self-condensation are prevented by the use of a monodentate anchoring group. We note that the hydroxyl groups on the surface have not been optimized as reported to be crucial for SiO_2. Still we observe proper SAM formation, which could suggest that the microstructure is an umbrella motif consisting of a 2D ordered densely packed monolayer directly attached to the blank polymer substrate.

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Supporting Information Available. Details on contact angles, XPS, and X-ray reflectivity. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481.
(2) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92.
(3) Ulman, A. *Self-assembled monolayers of Thiols*; Academic Press: San Diego, CA, 1998; Vol. 24.
(4) de Boer, B.; Hadipour, A.; Mandoc, M. M.; van Woudenbergh, T.; Blom, P. W. M. *Adv. Mater.* **2005**, *17*, 621.
(5) Mathijssen, S. G. J.; van Hal, P. A.; van den Biggelaar, T. J. M.; Smits, E. C. P.; de Boer, B.; Kemerink, M.; Janssen, R. A. J.; de Leeuw, D. M. *Adv. Mater.* **2008**, *20*, 2703.
(6) Akkerman, H. B.; Blom, P. W. M.; de Leeuw, D. M.; de Boer, B. *Nature* **2006**, *441*, 69.
(7) DiBenedetto, S. A.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *Adv. Mater.* **2009**, *21*, 1407.
(8) Klauk, H.; Zschieschang, U.; Pflaum, J.; Halik, M. *Nature* **2007**, *445*, 745.
(9) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418.
(10) Smits, E. C. P.; Mathijssen, S. G. J.; van Hal, P. A.; Setayesh, S.; Geuns, T. C. T.; Mutsaers, K. A. H. A.; Cantatore, E.; Wondergem, H. J.; Werzer, O.; Resel, R.; Kemerink, M.; Kirchmeyer, S.; Muzafarov, A. M.; Ponomarenko, S. A.; de Boer, B.; Blom, P. W. M.; de Leeuw, D. M. *Nature* **2008**, *455*, 956.
(11) Onclin, S.; Ravoo, B. J.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **2005**, *44*, 6282.
(12) Xiang, J.; Zhu, P.; Masuda, Y.; Koumoto, K. *Langmuir* **2004**, *20*, 3278–3283.
(13) Chaudhury, M. K. *Biosens. Bioelectron.* **1995**, *10*, 785.
(14) Calhoun, M. F.; Sanchez, J.; Olaya, D.; Gershenson, M. E.; Podzorov, V. *Nat. Mater.* **2008**, *7*, 84.
(15) Ulman, A. *Organic Thin Films and Surfaces: Directions for the Nineties in Thin Films* Academic Press: San Diego, CA, 1995; Vol. 20, p 85.
(16) de Leeuw, D. M.; Gelinck, G. H.; Matters, M. US Patent 6635406, 2003.
(17) Kim, H. S.; Plis, E.; Khoshakhlagh, A.; Myers, S.; Gautam, N.; Sharma, Y. D.; Dawson, L. R.; Krishna, S.; Lee, S. J.; Noh, S. K. *Appl. Phys. Lett.* **2010**, *96*, No. 033502.
(18) Cantatore, E.; Geuns, T. C. T.; Gelinck, G. H.; van Veenendaal, E.; Gruijthuijsen, A. F. A.; Schrijnemakers, L.; Drews, S.; de Leeuw, D. *IEEE J. Solid-State Circuits* **2007**, *42*, 84.

DOI: 10.1021/nl9032268 | *Nano Lett.* **2010,** *10,* 1998–2002

(19) Ferguson, G. S.; Chaudhury, M. K.; Biebuyck, H. A.; Whitesides, G. M. *Macromolecules* **1993**, *26*, 5870.
(20) Yoneda, Y. Anomalous surface reflection of X-rays. *Phys. Rev.* **1963**, *131*, 2010.
(21) Fenter, P. In *Self-Assembled Monolayers of Thiols*; Uhlman, A., Ed.; Academic Press: San Diego, CA, 1991.
(22) Fichou, D. *Handbook of Oligo- and Polythiophenes*; Wiley-VCH: Weinheim and New York, 1999.
(23) Mathijssen, S. G. J.; Smits, E. C. P.; van Hal, P. A.; Wondergem, H. J.; Ponomarenko, S. A.; Moser, A.; Resel, R.; Bobbert, P. A.; Kemerink, M.; Janssen, R. A. J.; de Leeuw, D. M. *Nat. Nanotechnol.* **2009**, *4*, 674.
(24) Spijkman, M.; Smits, E. C. P.; Blom, P. W. M.; de Leeuw, D. M.; Bon Saint Come, Y.; Setayesh, S.; Cantatore, E. *Appl. Phys. Lett.* **2008**, *92*, 143304.
(25) Cantatore, E.; Meijer, E. J. In *ESSCIRC 2003, Proceedings of the 29th European Solid State Circuits Conference*, 2003.
(26) Gelinck, G. H.; Huitema, H. E. A.; van Veenendaal, E.; Cantatore, E.; Schrijnemakers, L.; van der Putten, J. B. P. H.; Genus, T. C. T.; Beenhakkers, M.; Giesbers, J. B.; Huisman, B. H.; Meijer, E. J.; Benito, E. M.; Touwslager, F. J.; Marsman, A. W.; van Rens, B. J. E.; de Leeuw, D. M. *Nat. Mater.* **2004**, *3*, 106.

DOI: 10.1021/nl9032268 | *Nano Lett.* **2010,** *10,* 1998--2002